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NRL Report 5792

# **THERMOELECTRIC INSTABILITY OF SOME NOBLE METAL THERMOCOUPLES AT HIGH TEMPERATURES**

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## ABSTRACT

Thermoelectric instabilities of noble metal thermocouples and individual thermoelements (platinum, rhodium, iridium, iridium-50% rhodium, and several platinum-rhodium alloys) have been studied from 1000° to 1700°C under oxidizing and neutral atmospheres. The principal source of instability was found to be a contamination of the thermoelements by impurities from ceramic protection tubes. Several grades of alumina sheathing were tested, and thermocouple errors associated with each grade were determined. With alumina sheathing the principal contaminant was iron, and the instability generated was at least an order of magnitude greater in a neutral atmosphere than in an oxidizing atmosphere. Increasing the wire size increases stability in a neutral atmosphere, although not in an oxidizing atmosphere. Instability increases rapidly with temperature between 1000° and 1700°C, but the order of decreasing stability remains Pt-6%Rh/Pt-30%Rh, Pt-1%Rh/Pt-13%Rh, and Pt/Pt-10%Rh or Pt/Pt-13%Rh. The instability of pure rhodium thermoelements, and of Ir and Ir-50%Rh thermoelements, depends on internal changes, and not as much on iron contamination as the Pt-Rh series of thermoelements; hence the pure rhodium and the iridium thermoelements become preferable if gross iron contamination is expected. When compositional changes are expected in a thermoelement, immersion depth should be maintained constant or increased.

## PROBLEM STATUS

This is a final report on one phase of this problem; work is continuing on other phases.

## AUTHORIZATION

NRL Problem C05-08  
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## **THERMOELECTRIC INSTABILITY OF SOME NOBLE METAL THERMOCOUPLES AT HIGH TEMPERATURES**

### **INTRODUCTION**

This laboratory is engaged in the measurement of thermal properties from 1000° to 1800°C. At these temperatures, where material compatibility is readily attainable, thermocouples offered the most promise for precise temperature determinations over extended periods. However, the reliability above 1000°C of even the most common thermocouple, Pt/Pt-10%Rh, could not be predicted from available published work.

Since many applications require thermocouples for use in both oxidizing and neutral atmospheres, the present investigation has been restricted to noble metal thermocouples, including combinations of Pt, Pt-Rh alloys, Ir, and Ir-50%Rh. It is recognized that many thermocouples with a refractory metal in one or both legs also offer promise in the specified temperature range.

In choosing a suitable thermocouple combination for a particular high temperature application, wires can generally be found that fulfill initial requirements such as melting point, ductility, thermoelectric output, chemical homogeneity, and material compatibility. However, the reliability of a particular thermocouple when used for extended periods is largely determined by the thermoelectric stability of each element, and information in this area is meager.

The purpose of this investigation was to study the factors which influence the stability of noble metal thermocouples and to provide sufficient information to allow predictions of the reliability of particular thermocouples under specified conditions. Several other investigators have reported measurements on the stability of noble metal thermocouples (1-4), but, in general, these studies are restricted and contradictory. Often this has resulted from a lack of control over factors such as immersion depth and environmental contamination.

The instability (change in output with time) of a thermocouple at constant immersion is normally associated with compositional changes in the thermal gradient zone of each element. These changes may result from contamination by furnace atmosphere or ceramic protection tubes, from exchange of alloying elements at the welded junction, or from preferential volatilization of one metal (or oxide) from the alloy leg. The magnitude of the compositional change which contributes to instability may also be influenced by time, temperature, atmosphere, wire size, and other geometry effects.

In this study, when thermocouples were given positive protection from furnace environment, impurities in ceramic protection tubes were found to be the principal source of contamination and consequent thermoelectric instability at high temperatures. Among the presently available ceramic materials for couple protection in the temperature range from 1000° to 1800°C, beryllia, alumina, and magnesia are attractive because of their high melting points, excellent thermal stabilities, and high electrical resistivities. The availability and prevalent use of alumina prompted its choice as a starting point in this investigation, and the contamination tests have been limited to wires sheathed in various grades of alumina.

### **EXPERIMENTAL METHOD**

To study the stability of a particular thermocouple under specified conditions, two general procedures have been used in previous investigations. The first involves the calibration of the complete thermocouple or an individual leg at some known reference

temperature (reference thermocouple or standard melting point metal), then heating for a given time under specified conditions, and again calibrating at the same reference temperature. The second method involves the use of a "referee" wire which can be joined to or removed from a permanent junction with several wires under test. Test wires may be given heat treatment while the referee is removed. When the referee is rejoined, thermoelectric changes in the test wires are measured.

The first of these procedures has an obvious disadvantage. Since the net potential of a thermocouple originates in the region of thermal gradient and thermoelectric instability results generally from induced chemical inhomogeneity in this region, immersion and gradient zones for both the firing tests and calibration tests must be exactly duplicated. This is very difficult in practice, and the conflicting results of many investigators may be traced to a lack of attention to these details.

In the second procedure, gradient zones are maintained constant so long as firing and calibration tests are performed at the same temperature. A modified form of the referee method was used in the present investigation. Modifications were made to permit positive isolation of each test wire from external furnace contamination and to provide for a direct measurement of the distribution of thermoelectric changes along each wire.

The procedure may be described as follows: A sheathed thermocouple or single leg was inserted into a furnace at a predetermined temperature and immersion depth and heated for a specified time. Upon removal from the furnace, each individual test leg was joined to a reference wire of the same material and the junction was pulled into the stability furnace (Fig. 1). Measurements were then made of the potential between the test wire and its reference at various positions along the test wire from the original thermocouple junction. If the test wire and reference were identical before heat treatment, observed readings represented actual deviations in the thermoelectric force of the test wire for a temperature difference of 860 degrees (the difference in temperature between the stability furnace and the room). Unheated portions of a test wire were always compared to the reference standard. Thus, any thermoelectric potential between the test wire and its reference, generated by chemical or physical inhomogeneity, was readily detectable, and the stability test would then be adjusted accordingly. In practice, if unheated test wires and reference wires were taken from the same lot, they were generally identical within  $\pm 2$  microvolts.

Since alumina protection tubes generally possess some permeability to gases at high temperatures, valid stability tests required positive protection of test wires from furnace atmosphere contamination and from cross-contamination with adjacent test wires. Each test wire or thermocouple was individually protected during firing by three alumina tubes - a test sheathing inside a closed-end tube of the same material, and an outer closed-end tube of high purity alumina. Inner sheathings were generally closed by fusing single-bore tubes and by capping double-bore tubes.

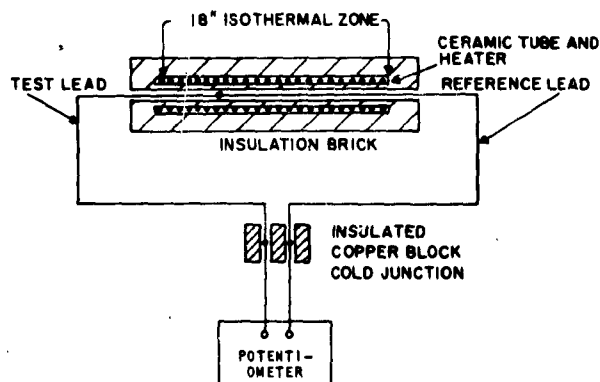


Fig. 1 - Measurement arrangement for the stability tests

## EXPERIMENTAL RESULTS

Instability Tests of Thermoelements of Platinum and  
Platinum-Rhodium Alloys in Alumina Sheathing in Argon

Thermoelectric changes at  $860^{\circ}\text{C}$  (relative to  $0^{\circ}\text{C}$ ) for individual elements of Pt and Pt-Rh alloys, sheathed in various grades of alumina and fired for 120 hours at  $1380^{\circ}\text{C}$ , are shown in Fig. 2. Since instability was found to be a function of wire size, all tests were made with 20-mil wire. For each grade of alumina sheathing, maximum changes in the noble metals are plotted as a function of the percent rhodium in the wires. The furnaces used for firing tests had isothermal zones of approximately three inches, and the plotted change, in each case, represents the maximum observed deviation in the thermal emf at  $860^{\circ}\text{C}$  for that portion of wire subjected to full firing temperature.

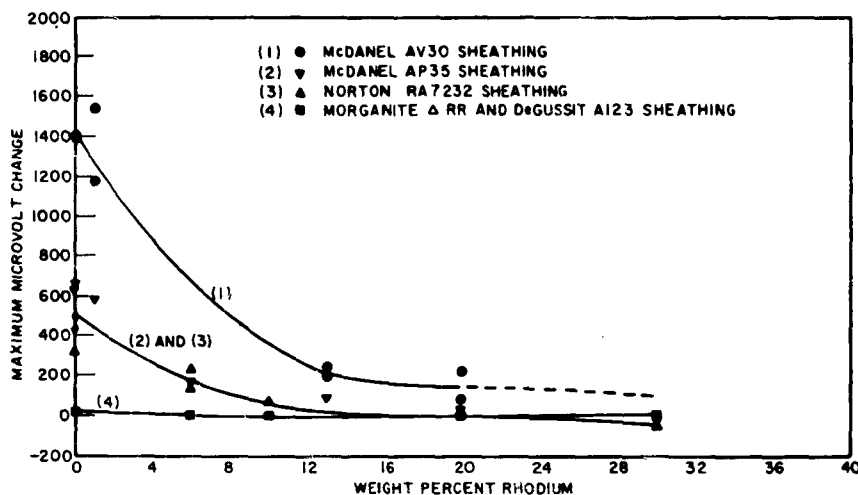


Fig. 2 - Maximum thermoelectric changes at  $860^{\circ}\text{C}$  for individual elements (20-mil size) of Pt and Pt-Rh alloys sheathed as indicated and fired for 120 hours at  $1380^{\circ}\text{C}$  in argon

The sign convention used for the data in Fig. 2, and for subsequent data in this report, follows the generally accepted form. When a negative charge is generated at the cold end of a thermoelement, the thermoelectric change is designated negative; and, when generated at the hot end, is designated positive. When two legs are joined to form a thermocouple, this convention dictates that a positive change in emf (in the thermal gradient zone) of that leg attached to the negative post of the potentiometer will decrease the emf of the couple, while a positive change in the other leg attached to the positive post will increase the emf of the couple.

Test wires and reference wires were of the highest grades obtainable and were always prefired electrically for 1/2 hour at  $1450^{\circ}\text{C}$ . Although prefiring produced no significant changes in the emf outputs of Pt and Pt-Rh wires, a standard practice of firing all test wires was adopted. Prefiring in this fashion could effect equalization of any physical and chemical inhomogeneity in the wires and also aid in the removal of any volatile impurities.

Several experiments were performed with platinum and alloy wires to establish that the observed changes in emf at  $1400^{\circ}\text{C}$  were not associated with physical or chemical changes in the wires themselves (for example, volatilization of one component or impurities



from the wires). The electrical heating of several bare wires of Pt and Pt-Rh at 1450°C for periods of 24 to 48 hours produced no measurable changes in emf. Excessive grain growth (produced in platinum wires by firing to the destruction point) and excessive cold working (produced by drawing wires repeatedly across rounded surfaces) did not change the thermal emf of the wires. Platinum wires which had been excessively cold worked and fired at 1400°C for 24 to 120 hours were also identical with unfired wires. Two platinum wires of 15-mil diameter were sheathed in closed-end quartz tubing of small internal diameter, positioned in DeGussit Al23 pyrometer tubes, and fired for 120 hours at 1350°C in argon. No thermoelectric changes larger than 2 microvolts were observed in these wires.

For Pt and Pt-Rh thermoelements, firing experiments with bare wires and with wires sheathed in relatively inert quartz and DeGussit Al23 (Fig. 2) have shown that chemical or physical changes in the wires themselves do not contribute to thermoelectric instability below 1400°C. The careful protection of all wires during firing tests has been described. The effectiveness of this protection against furnace contamination up to 1400°C was demonstrated by the similarity of data obtained under different furnace environments. Firing furnaces have been used with both molybdenum and Pt-40%Rh heaters and with both zirconia and alumina bubble as insulation. There has been no significant difference in the stabilities of like thermoelements fired in different furnaces. It was concluded that the principal contaminant (or contaminants) which contributed to the observed instability was picked up from the protective sheathing.

At temperatures above 1500°C, it was more difficult to establish the stability of bare wires. Long term firing of unsupported wires at 1700°C was not possible since the wires burned out after several minutes when heated electrically at this temperature. However, any major change in a bare wire would be expected to occur in the alloy leg by the preferential volatilization of one component, and it will be shown later in this report that emf changes are very minor for Pt-Rh wires when they are supported by a very pure alumina and heated for 120 hours in argon at 1660°C or in air at 1730°C.

Several experiments were made to determine the effect of wire size on the thermoelectric instability resulting from impurities in alumina. The maximum emf changes at 860°C for 5, 10, and 20 mil platinum wires, when sheathed in McDanel AP35 and fired at 1380°C for 120 hours, were 2825, 1053, and 325 microvolts, respectively. It is significant that the contamination increased with a decrease in wire size at a rate approximately midway between the rate predicted by diameter ratios and that predicted by cross-sectional-area ratios.

The transfer of impurities from alumina to the wires would be possible by at least two general mechanisms. If contamination does not require physical contact between the noble metal and the alumina, the reduction or decomposition of a metal compound must occur with subsequent vaporization of the metal impurity to the wire. If, on the other hand, contact between the wire and alumina is required, the noble metal could reduce the metal compound with subsequent diffusion of the metal impurity into the wire. Although the exact mechanism has not been determined, some relevant information will be presented later in this report.

Polycrystalline alumina is generally contaminated with iron, silicon, sodium, calcium, and magnesium, with lesser amounts of copper, silver, manganese, nickel, and tin. These impurities probably occur as mixed oxides. Of the major contaminants only iron, silicon, and sodium compounds are likely to be thermodynamically unstable. Published studies have shown that platinum wires may be contaminated by either silicon or iron. Contamination and embrittlement of platinum by silicon compounds (5) in the presence of sulfur and other reducing agents have been established. Bennett (6) reported that Pt-Rh wires when heated in refractory powders at 1200°C became contaminated with iron.

A logical step in identifying the active contaminant was to compare the iron and silicon contents of the various grades of alumina with the corresponding instabilities for a particular noble metal wire. Representative samples of each grade of alumina were analyzed chemically for iron and silicon. The analyses were performed by two independent groups at this laboratory and are presented in Table 1. The alumina grades with high iron contents also have high silicon contents, and the emf instability of Pt or any chosen alloy can be correlated equally well with either the iron content or the silicon content.

Table 1  
Analyses for Iron and Silicon in Various Grades of Alumina Sheathing

Grade	Chemistry Div. NRL		Metallurgy Div. NRL	
	Fe (wt-%)	Si (wt-%)	Fe (wt-%)	Si (wt-%)
McDanel AV30	0.18	2.70	0.18	3.59
McDanel AP35	0.07	1.05	0.067	1.15
Norton RA 7232	0.11	0.56	0.064	0.67
DeGussit A123	<0.04	0.14	0.034	0.10
Morganite ΔRR	<0.04	0.13	0.022	0.05

A clue to the contaminant responsible for instability was provided by spectrographic analyses of Pt and Pt-Rh wires before and after firing for 120 hours in a sheathing of high iron content. The iron content of all wires was strongly increased by firing, and for platinum was a rough function of the degree of instability. There was also an increase in the copper and aluminum content of most wires, but always at least one order of magnitude less than that of iron. No pickup of either silicon or sodium, within the limits of the analytical method, could be detected. Platinum wires, tested before and after contamination in sheathings of low iron content, still exhibited an increase in copper and aluminum but no detectable pickup of iron.

To further identify iron, as opposed to silicon, as the active contaminant responsible for thermoelectric instability, several additional experiments were performed. Platinum wires (15-mil diameter) were coiled, embedded in various metal oxide powders, and electrically fired at 1400°C in argon for 24 hours. The wires were then uncoiled and tested for instability against reference standards. The results of these tests are presented in Table 2. Since the purities of the powdered oxides were not controlled, the small changes for wires heated in zirconia, magnesia, alumina, silica, and calcium oxide are not significant. Although the combined form of iron in the sheathing is not known, the large change observed for platinum heated in  $\text{Fe}_2\text{O}_3$  does point to iron as the active impurity in alumina.

The possibility that an interaction of silica with iron (or with another impurity in the solid sheathing) could have released trace silicon, which may not have been detected in the spectrographic tests on wires, prompted several additional experiments. Powdered mixtures, prepared by mixing finely divided alumina (0.04% Fe and 0.15% Si) without additions and with known additions of  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$ , were poured around concentric platinum wires in pyrometer tubes of low iron content. The wire-powder systems were then sintered and fired for 120 hours at 1380°C in argon, and the wires checked for change in the thermal emf.

Table 2  
Thermoelectric Instability of Platinum Wires Fired in Powdered  
Oxides at 1400°C for 24 Hours (Argon Atmosphere)

Metal Oxide Powder	Maximum Thermoelectric Change at 860°C ( $\mu$ v)
Zirconia ("I" Insulating Grade)	+ 42
Magnesia (Reagent Grade)	+ 22
Alumina (90 mesh; 0.02% Fe and 0.00% Si)	+ 21
Calcium Oxide (Reagent Grade)	+ 34
Silica (Reagent Grade)	+ 17
Ferric Oxide (Reagent Grade)	+ 3840

The pure alumina powder had an iron content equivalent to that of the purest sheathing, but platinum wires fired in this powder with no addition of Si or Fe exhibited large emf changes and gross contamination. It is apparent that diffusion and transfer of iron from the low density, sintered compact to the wire is undoubtedly much easier than from a high density sheathing to the wire. The natural iron content of the alumina powder (0.04% Fe) appeared to provide saturation, since wires fired in powders of higher iron content (0.18% Fe) exhibited emf changes of like magnitude. In two experiments,  $\text{SiO}_2$  (2.7% Si) was added to powders containing 0.04% and 0.18% Fe. It is significant that wires fired in these compacts exhibited emf changes significantly lower (one-third) than those observed in similar compacts with no addition of silicon. Although these experiments were strongly influenced by geometry factors, they do provide evidence that iron and not silicon is the active contaminant in the alumina sheathing.

The mechanism by which iron reaches the noble metal wire is undoubtedly complex. Although no attempt was made to identify the exact mechanism, some practical information was obtained. Experimentally, it was shown that the noble metal (in neutral atmosphere) does not have to be in contact with the insulation for contamination to occur. Platinum wires were coiled on sapphire and DeGussit Al23 rods, inserted centrally in pyrometer tubes of high iron content, and heated for 120 hours at 1400°C. The emf changes measured for these wires were associated with the high iron content of the pyrometer tube rather than the low iron content of the rods. It would appear that the general mechanism in a neutral atmosphere must involve a reduction or decomposition of the iron compound in the insulation, with subsequent vaporization of metallic iron to the noble metal wires. The volatility of iron permits this mechanism, and its vapor pressure can be roughly correlated with the change in stability with temperature for a particular grade of alumina.

For a given grade of alumina (Fig. 2) the emf change in a wire due to iron contamination is a maximum for pure Pt and falls in a well-defined manner to a small negative value for Pt-30%Rh. This could suggest a decreased contamination of the alloy wire, but the spectrographic tests indicated that Pt and Pt-Rh wires, when fired under like conditions, were contaminated to the same degree by iron. Thermal emfs for Pt and for alloys in the Pt-Rh series have been accurately determined, and it can be readily shown that an instability curve resembling those in Fig. 2 would be obtained by the addition of equal amounts of Rh to Pt and Pt-Rh alloys. Since the absolute thermal emfs of iron and rhodium are of the same magnitude (7), the analogous effect of iron is understandable.

For pure rhodium, the proportion of the instability caused by iron contamination could not be determined, since a stabilization of bare rhodium wire could not be attained. This

instability of rhodium was only studied to a limited degree and could be due to the loss of impurities from the wire or to the existence of two rhodium phases. According to Rudnitskii (3), rhodium does exist in two modifications with a transformation temperature at  $1030^{\circ}\text{C}$ . This does not necessarily eliminate rhodium as a reliable thermoelement, since the maximum shift observed (for 216 hours at  $1400^{\circ}\text{C}$  in an alumina of high iron content) was only -80 microvolts. The Pt-30%Rh alloy (Fig. 2) also exhibits a small negative change, and it is suspected that emf changes for compositions with rhodium contents greater than 30% are also in the low negative range.

The influence of temperature on contamination and instability is illustrated in Fig. 3. Thermoelectric changes, measured at  $860^{\circ}\text{C}$ , for individual elements of Pt and Pt-Rh alloys, sheathed in an alumina of low iron content and fired for 120 hours at  $1380^{\circ}$  and  $1660^{\circ}\text{C}$ , are plotted as a function of rhodium content. At  $1380^{\circ}\text{C}$ , Pt and all the Pt-Rh alloys exhibit practically no emf change; however, at the higher temperature, platinum and the alloys of low rhodium content again exhibit significant changes.

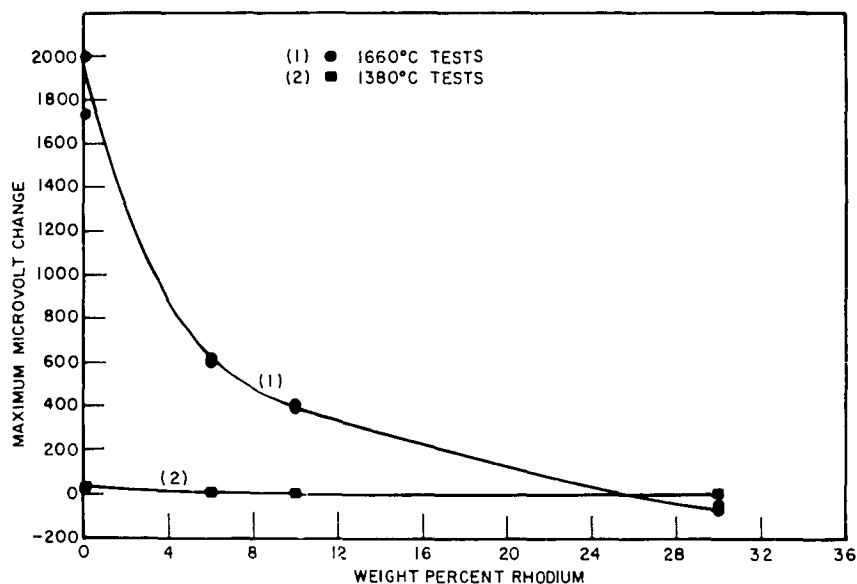


Fig. 3 - Maximum thermoelectric changes at  $860^{\circ}\text{C}$  for individual elements (20-mil size) of Pt and Pt-Rh alloys sheathed in DeGussit Al23 and fired for 120 hours at the indicated temperatures in argon

#### Instability Tests of Thermoelements of Iridium and Iridium-50% Rhodium in Argon

The maximum emf changes, measured at  $860^{\circ}\text{C}$ , for the Ir and Ir-50%Rh elements, when sheathed in two grades of alumina (McDaniel AV30 and DeGussit Al23) and fired for 120 hours at  $1380^{\circ}$  and  $1660^{\circ}\text{C}$ , are presented in Table 3. The resistance to contamination exhibited by these thermoelements, particularly iridium, is apparent. The magnitude of the emf change generated in Ir-50%Rh at  $1380^{\circ}\text{C}$  did change when the wire was incased in a sheathing of high iron content; but the rapid increase in instability with increasing iron content of the sheathing, observed with the platinum-rhodium series, was not evident. The mechanism which causes emf instability in these elements will be discussed after studies in air have been presented.

Table 3  
Instability Tests of Individual Elements of Iridium  
and Iridium-50% Rhodium in Argon

Insulation Grade	Element	Wire Size (mils)	Firing Temp. (°C)	Maximum Emf Change at 860°C (μv)	
				Fired 120 Hr	Fired 216 Hr
McDanel AV30	Ir	20	1380	+13	+33
McDanel AV30	Ir-50%Rh	20	1380	-142	-303
McDanel AP35	Ir	20	1380	+37	-
McDanel AP35	Ir-50%Rh	20	1380	-10	-
DeGussit A123	Ir	20	1380	+33	-
DeGussit A123	Ir-50%Rh	20	1380	+35	-
DeGussit A123	Ir	20	1660	+47	-
DeGussit A123	Ir-50%Rh	20	1660	-154	-

Wires of Ir and Ir-50%Rh were prefired in argon at 1900° and 1800°C, respectively, for 1 minute. The brief prefiring produced no significant changes in the emf output of the wires. However, wires of these materials did not have the homogeneity observed with the Pt-Rh series, and thermoelectric variations as high as ±5 and ±10 microvolts were observed along 4-foot lengths of Ir and Ir-50%Rh wires, respectively.

These elements were not studied in detail; factors such as wire size and geometry were not investigated. Several firing tests on bare wires were conducted in argon at 1400°C. For these short term tests (24 hours), neither element exhibited emf changes in excess of those expected from the inhomogeneity in the wires.

#### Instability Tests of Thermocouples in Alumina Sheathing in Argon

Chaussain (1) noted, with platinum wires, that the thermal emf change induced by contamination was linear with temperature. In the present investigation, wires were generally tested for instability by comparison with referees at 860°C. However, emf changes of several contaminated wires (Pt, Ir, Ir-50%Rh, and Pt-Rh alloys) were measured by the referee technique at several temperatures between 400° and 1400°C. These tests verified that the emf change generated in any of the noble metal wires by contamination was, effectively, a linear function of temperature regardless of the degree of contamination. Therefore, the absolute thermal emf  $\alpha$  (microvolts/°C) generated by a given degree of contamination should have the same value at any temperature. The stability test used in this investigation measured  $\alpha$  along the length of each couple leg. By additional measurements of the temperature gradients along the wires at any predetermined temperature of the firing furnace, it was convenient to calculate the net emf change in microvolts for a given thermocouple when fully immersed by integrating with the following equation over contaminated lengths of both legs:

$$\Delta E = \int_{t_1}^{t_2} (\alpha_x^+ - \alpha_x^-) dt$$

where

$\Delta E$  is the net emf change of the thermocouple reading

$t$  is the temperature of both legs in the gradient zone at a distance  $x$  from the junction

- $\alpha_x^+$  is the absolute thermal emf of contamination for the leg attached to the positive pole of the potentiometer at a distance  $x$  from the junction
- $\alpha_x^-$  is the absolute thermal emf of contamination for the leg attached to the negative pole of the potentiometer at a distance  $x$  from the junction.

Comparisons of the emf instabilities of several thermocouple pairs, sheathed in different grades of alumina and fired in argon, are presented in Table 4. Each instability figure reported in the table represents an average of two or more experimental values from tests at the same conditions. The net emf change of each thermocouple was calculated by the procedure outlined at the reduced temperature of 860°C after firing at constant immersion under specified conditions. The integration procedure required a measurement of the distribution of temperatures along the core of the firing furnace at this reduced temperature. Since the temperature error of a couple pair is determined by the induced deviation in degrees, integrated microvolt changes were converted to corresponding changes in degrees. For each thermocouple, the maximum change at the same reduced temperature of 860°C is also presented to illustrate the error which could be generated by decreasing the immersion after firing. Since the absolute thermal emf (microvolts/°C) of a given contamination was shown to be constant with change in temperature (at least to 1400°C), the maximum change in microvolt units will be approximately proportional to temperature and can be estimated at other temperatures.

To check the effectiveness of the integration procedure for calculating net changes at constant immersion, calibration shifts at 860°C for several thermocouples, which had been fired at 1380°C for 216 hours at constant immersion, were observed by the standard referee technique and compared to corresponding calculated changes. The observed and calculated values are compared in Table 4 and are in reasonable agreement. Since the integration procedure gave the proper magnitudes for instability, this procedure in preference to the more time-consuming referee technique was adopted for the majority of the tests.

Since the instability tests permitted a measurement of the distribution and magnitude of emf changes in the individual couple wires as a function of distance from the couple weld, junction effects could be distinguished from contamination and studied independently. Stability experiments were made for individual elements and for welded combinations after firing at 1380° and 1660°C in argon. Transfer of a metal from one leg to the other by diffusion or vaporization could contribute to the instability of a thermocouple. The distribution and magnitude of emf changes, however, in individually fired wires and in those fired in joined combination were normally identical, and no junction effects for the various thermocouple combinations were detected beyond an inch from the welded junctions.

The direct influence of wire size on contamination has been discussed, and the majority of the tests in Table 4 were made with 20-mil wires. The geometry factor (involving wire, sheathing, and contact areas) with its influence on the degree of contamination and the movement of contamination along the wire is probably very complex. An attempt was made to equalize this factor for all experiments by using standard 12-inch sheathing of 1/32-inch bore. Even this practice, however, did not prevent an influence of geometry and time on the distribution of contaminant along the various wires. This is evident in Table 4 by the lack of uniformity in the ratio of the maximum change to the net change at constant immersion. After 120 hours at 1380°C, an appreciable emf change in a wire was normally observed 2 to 5 inches above the isothermal zone of the firing furnace and, after 216 hours, up to 6 and 7 inches above the isothermal zone.

The net emf change with time (Table 4) was effectively linear for all the couple combinations up to 216 hours. This linear change would not be expected to continue as the contaminant content in the insulation becomes depleted. This was observed for a 20-mil

Table 4  
Instability Changes for Various Thermocouple Pairs as a Function of Time, Temperature,  
and Immersion for Several Grades of Alumina (Argon Atmosphere)

Insulation Grade	Couple Pair	Wire Sizes (mils)	Firing Temp. (°C)	Instability Change at 860°C After Firing at Constant Immersion (°C)				Maximum Instability Change at 860°C Which Could be Generated by Decreasing the Immersion After Firing (°C)			
				Fired 120 Hr		Fired 216 Hr		Fired 120 Hr	Fired 216 Hr	Fired 120 Hr	Fired 216 Hr
				Obs'd	Calc'd	Obs'd	Calc'd				
McDanel AV30	Pt/Pt10Rh	12	1380	-20*	-	-40	-29	-	-	-	-231
	Pt/Pt10Rh	15	1380	-	-11	-	-	-133	-	-	-
	Pt/Pt10Rh	15	1000	-	<0.2	-	-	-0.5	-	-	-
	Pt/Pt13Rh	20	1380	-10*	-	-18	-17	-	-	-180	-
	Pt1Rh/Pt13Rh	20	1380	-11*	-5	-20	-26	-58	-	-215	-
	Rh/Pt20Rh	20	1380	-12*	-	-20	-19	-	-	-43	-
McDanel AP35	Ir/Ir50Rh	20	1380	-2*	-2	-3	-5	-23	-	-56	-
	Pt/Pt10Rh	20	1380	-	-10	-	-	-83	-	-	-
	Pt/Pt20Rh	20	1380	-	-7	-	-	-49	-	-	-
	Pt1Rh/Pt13Rh	20	1380	-	-6	-	-	-46	-	-	-
	Pt6Rh/Pt30Rh	20	1380	-	-4	-	-	-24	-	-	-
	Pt/Rh	20	1380	-	-2	-	-	-15	-	-	-
Norton RA 7232	Ir/Ir50Rh	20	1380	-	-1	-	-	-8	-	-	-
	Pt/Pt10Rh	15	1380	-	-7	-	-	-48	-	-	-
	Pt/Pt10Rh	20	1380	-	-4	-	-	-33	-	-	-
	Pt6Rh/Pt30Rh	20	1380	-	-7	-	-	-26	-	-	-
	Pt/Pt10Rh	10	1380	-	-2	-	-	-12	-	-	-
	Pt/Pt10Rh	20	1380	-	-1	-	-	-3	-	-	-
Morganite ΔRR	Pt/Pt20Rh	20	1380	-	<0.2	-	-	-1	-	-	-
	Pt/Pt10Rh	15	1380	-	-1	-	-	-4	-	-	-
	Pt/Pt10Rh	20	1380	-	<0.5	-	-	-3	-	-	-
	Pt6Rh/Pt30Rh	20	1380	-	<0.2	-	-	-1	-	-	-
	Ir/Ir50Rh	20	1380	-	<0.2	-	-	+1	-	-	-
	Pt/Pt10Rh	15	1660	-	-22	-	-	-187	-	-	-
DeGussit Al23	Pt6Rh/Pt30Rh	20	1660	-	-10	-	-	-82	-	-	-
	Ir/Ir50Rh	20	1660	-	-3	-	-	-39	-	-	-

\*Estimated by comparing couple temperatures with optical pyrometer observations at 12-hour intervals when firing at 1380°C.

Pt/Pt-10%Rh thermocouple which was used for 720 hours in McDanel AV30 alumina at 1380°C. This couple exhibited a change in calibration of 40°C for the first 360 hours and only 10°C for the last 360 hours.

#### Instability Tests of Thermoelements of Platinum and Platinum-Rhodium Alloys in Alumina Sheathing in Air

Emf changes for individual elements of platinum and platinum-rhodium alloys, sheathed in various grades of alumina and fired for 120 hours at 1380°C in air, are shown in Fig. 4. For each grade of alumina sheathing, maximum emf changes (at 860°C) for the noble metal wires are plotted as a function of the rhodium content in the wires. The similarity of the shape of these curves with those obtained under a neutral atmosphere (Fig. 2) is apparent. Although in air the changes are several orders of magnitude lower than those in argon, the stabilities of all wires again increase with increasing purity of the alumina (or decreasing iron content). The influence of temperature on instability in an oxidizing atmosphere is illustrated in Fig. 5. Maximum emf changes for individual elements, sheathed in DeGussit Al23 and fired for 120 hours at 1380° and 1730°C are again plotted as a function of rhodium content. Though no emf changes were detected at 1380°C for wires sheathed in Morganite  $\Delta$ RR or DeGussit Al23, significant deviations were observed at the higher temperature.

The dependency of contamination on wire size, noted in argon experiments, was not apparent in air. Instability tests were made for several sizes of Pt and Pt-10%Rh wires, sheathed in McDanel AV30 and fired for 120 hours at 1380°C. For wires 5, 10, 15, and 20 mils in diameter, observed instabilities were identical

The low magnitude of the air contamination made identification of the active contaminant in the insulation very difficult. Spectrographic tests were again made on wires before and after firing. For wires sheathed in an alumina of high iron content and fired at 1380°C the tests showed a pickup of Fe, Al, and Cu with no Si or Na. For wires fired in sheathings of low iron content at the same temperature the tests showed a similar pickup of Al and Cu with no Fe, Si, or Na. This is good evidence that neither Al nor Cu contribute significantly to instability.

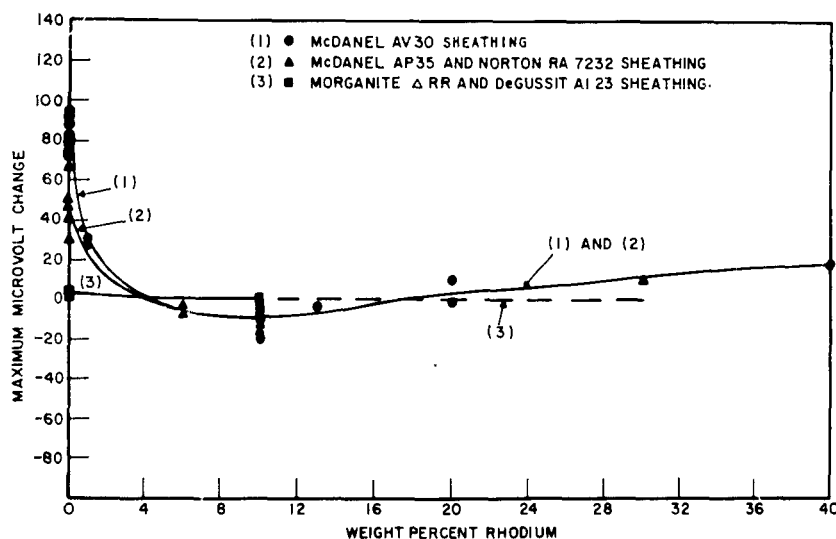


Fig. 4 - Maximum thermoelectric changes at 860°C for individual elements of Pt and Pt-Rh alloys sheathed as indicated and fired for 120 hours at 1380°C in air



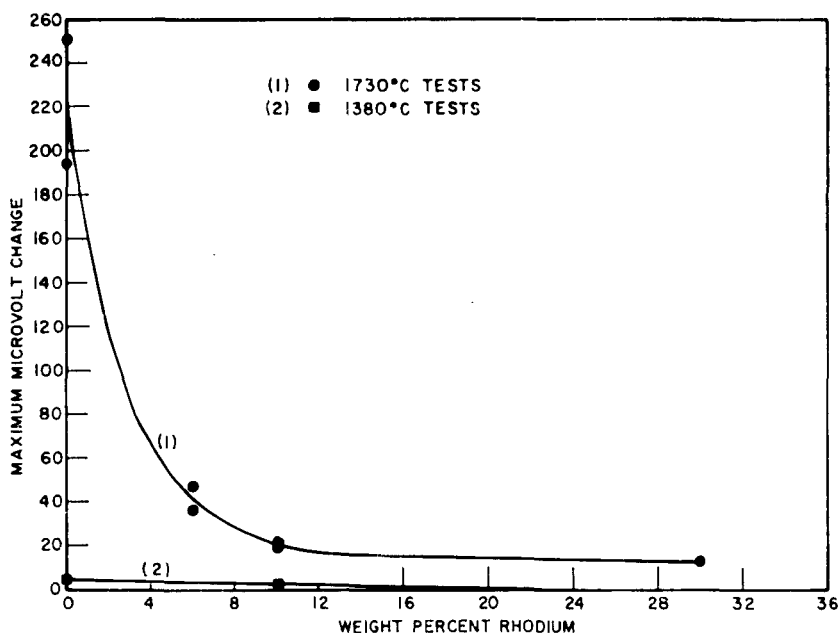


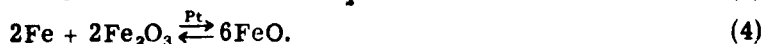
Fig. 5 - Maximum thermoelectric changes at 860°C for individual elements of Pt and Pt-Rh alloys sheathed in DeGussit Al23 and fired for 120 hours at the indicated temperatures in air

The direct relationship between observed instability in a neutral atmosphere and the iron content of the alumina sheathing has been shown. When maximum emf changes, generated in a given thermoelement (Fig. 4) after firing at 1380°C for 120 hours in air, are compared to the iron content in each grade of alumina (Table 1), a direct relationship between the instability in air and the iron content of the sheathing is again evident. On the basis of the spectrographic tests of wires fired in air and the similarity of contamination tests in air and argon it appears that iron is again the principal contributor to instability, at least to 1400°C.

Since wires fired in an alumina insulation of low iron content exhibited significant instability at 1730°C and since bare wire firing tests were not permitted above 1450°C, the possibility that physical and chemical changes may also occur in the wires at the higher temperatures has not been completely eliminated. However, preferential volatilization of either Pt or Rh from the alloy legs at 1730°C must be rather low as evidenced by the small emf changes for alloy wires fired in alumina of low iron content (Fig. 5). This fact and the similarity of the instability curves at 1380° and 1730°C (Figs. 4 and 5) suggest that instability at the higher temperature is also principally associated with impurities in the alumina, presumably iron.

It was surmised that in a neutral atmosphere iron reached the noble metal wires by the decomposition (or reduction) of an iron compound in the insulation with subsequent vaporization of metallic iron. The reduced contamination by iron in an oxidizing atmosphere by this mechanism is then understandable. The presence of free oxygen would tend to oxidize the iron and strongly inhibit both the decomposition and vaporization steps.

Baak and Hornyak (8) noted reactions of platinum with iron-containing silicates and determined that the interaction of iron with platinum proceeded through the following equations.



One would suspect that a contamination mechanism in air involving the reduction of iron oxides by platinum with subsequent diffusion of iron into the noble metal wires would require physical contact between the noble metal and the insulation. Experimentally this was shown to be only partially true. Platinum wires were coiled on sapphire rods, inserted in pyrometer tubes of high iron content, and heated for 120 hours at 1400°C in air. In contrast to similar experiments in a neutral atmosphere, emf changes were lower than those observed with wires in physical contact with the surrounding alumina. The apparent influence of physical contact between the insulation and the noble metal and the lack of geometry effects suggest that the contamination mechanism could involve both a reduction of iron compounds by the noble metal and a decomposition of the iron compounds in the insulation.

#### Instability Tests of Thermoelements of Iridium and Iridium-50% Rhodium in Air

Instability tests in air of individual elements of Ir and Ir-50%Rh when fired for 120 and 216 hours at 1380°C in McDanel AV30 and 120 hours at 1380° and 1730°C in DeGussit Al23 are presented in Table 5. As in previous tests of individual elements, the maximum microvolt change reported for each wire after firing was measured at 860°C.

Table 5  
Instability Tests of Individual Elements of Iridium  
and Iridium-50% Rhodium in Air

Insulation Grade	Element	Wire Size (mils)	Firing Temp. (°C)	Maximum Emf Change at 860°C (μv)	
				Fired 120 Hr	Fired 216 Hr
McDanel AV30	Ir	20	1380	-	+13
McDanel AV30	Ir-50%Rh	20	1380	-	+36
McDanel AP35	Ir	20	1380	+36	-
McDanel AP35	Ir-50%Rh	20	1380	+101	-
DeGussit Al23	Ir	20	1380	+28	-
DeGussit Al23	Ir-50%Rh	20	1380	+91	-
DeGussit Al23	Ir	20	1730	+39	-
DeGussit Al23	Ir-50%Rh	20	1730	+98	-

Thermoelectric changes observed for each element fired in air were lower than those observed at comparable temperatures in argon (Table 3), but the increased instability in a neutral atmosphere was not as noticeable as it was for the Pt-Rh series. In fact, iridium wires exhibited very small changes at 1380°C, which were practically independent of atmosphere, temperature, and grade of alumina sheathing. Similar emf changes of +14 to +26 microvolts have been observed for bare iridium wires when fired electrically at temperatures above 1350°C for 1-1/2 hours. Spectrographic tests of iridium wires, before and after firing, again suggest iron as the principal contaminant. Appreciable iron (if no com-

pound is formed) could be introduced into iridium to form an alloy with a thermoelectric force practically identical to that of iridium, since the absolute thermoelectric forces (7) for both metals are of the same magnitude.

When insulated elements of Ir-50%Rh were fired in air and in argon at the same temperature, the generated change in emf differed both in magnitude and direction. The change generated in this leg when fired in air also appeared to be independent of both the grade of insulation and the temperature, and emf changes of +25 to +41 microvolts have been observed in bare alloy wires when heated electrically in air at temperatures above 1350°C for 1-1/2 hours. The mechanisms causing instability have not been investigated. However, the shift in sign does suggest two competing mechanisms, possibly a contamination by iron or some other impurity and the preferential volatilization of iridium oxide or of an impurity from the alloy leg.

#### Instability Tests of Thermocouples in Alumina Sheathing in Air

Wires were generally tested for instability, after firing, by comparison with referees at 860°C. For tests in argon, it was shown that the emf change generated in each noble metal wire by contamination was effectively a linear function of temperature. Additional tests were made for wires contaminated in air by measuring emf change at several temperatures between 400° and 1400°C. These tests again verified that the emf changes generated in any of the noble metal wires by contamination in air was effectively a linear function of temperature regardless of the degree of contamination.

When thermocouples were contaminated by firing in argon, it was shown that net emf changes at constant immersion were effectively calculated by an integration of the apparent absolute emf along the gradient zone (Eq. 1). This procedure was simplified for the air experiments with Pt-Rh thermocouples at temperatures to 1400°C, since the degree of contamination (and the resulting emf change) at any point along the wire was a single function of temperature and was independent of wire size and other geometry factors.

It is apparent from Fig. 4 that effectively all the instability of a thermocouple in the Pt-Rh series arises in the pure platinum or low alloy leg. The microvolt changes generated in platinum wires, when fired for 120 and 240 hours in McDanel AV30 alumina, were determined for several firing temperatures between 1000° and 1400°C. These microvolt changes were compared to those generated at corresponding conditions along the gradient zone in fired platinum wires and were found to be identical for like temperatures and times. The distribution of contaminant was strictly a function of temperature, and the calibration change at constant immersion for any couple in the Pt-Rh series (to 1400°C) was calculable (Eq. 1) without knowledge of the linear distribution of temperatures in the gradient zone. For Pt-Rh tests at 1730°C and for all tests with the Ir-Rh thermocouple, the simplified procedure for calculating the emf change at constant immersion was not validated, and calculations were made with a measured distribution of temperatures in the gradient zone as previously described for couples in a neutral atmosphere.

A comparison of the emf instabilities (in degrees centigrade) of several thermocouple pairs, sheathed in different grades of alumina and fired in air, is presented in Table 6. The net emf change for each thermocouple at constant immersion was calculated by one of the two procedures outlined. Net changes were calculated at the temperature of firing except for couples fired at 1730°C for which net changes are reported at the reduced temperature of 1380°C. The corresponding maximum change in each couple is also presented to again illustrate the error which could be generated by decreasing the immersion after firing. Since the apparent absolute thermal emf of contamination is again constant with temperature (at least to 1400°C), the maximum microvolt change for a given thermocouple will be proportional to temperature, and the change at another temperature can be reliably estimated. The instabilities for thermocouples with pure rhodium in one leg represent net changes resulting from an iron contamination and from an unidentified instability in rhodium.

Table 6  
Instability Changes for Various Thermocouple Pairs as a Function of Time, Temperature,  
and Immersion for Several Grades of Alumina (Air Atmosphere)

Insulation Grade	Couple Pair	Wire Sizes (mils)	No. Tests	Temperature Hot Junction Immersion (°C)	Minimum Immersion to Avoid Error by Diffusion and/or Vaporization at Junction (in.)		Net Instability Change at Firing Temperature with any Constant Immersion (°C)		Maximum Instability Change at Firing Temperature Which Could be Generated by Decreasing the Immersion (°C)	
					120 Hr	240 Hr	120 Hr	240 Hr	120 Hr	240 Hr
McDanel AV30	Pt/Pt10Rh	5,10, 15,20	10	1384	<1	<1	-1.2 to -1.4	-1.2 to -1.4	-11.4	-11.4
	Pt/Pt10Rh	15	2	1230	<1	<1	-0.3	-0.3	-3.6	-3.6
	Pt/Pt10Rh	15	2	1000	<1	<1	0	0	<0.2	<0.2
	Pt/Pt13Rh	20	2	1384	<1	<1	-1.4	-1.4	-12.0	-12.0
	Pt1Rh/Pt13Rh	20	2	1384	<1	<1	-0.4	-0.4	-3.9	-3.9
	Pt6Rh/Pt30Rh	20	-	1384	-	-	<0.2*	<0.2*	-	-
McDanel AP35	Rh/Pt20Rh	20	2	1384	<2	<2	-3.5	-3.5	-6.6	-6.6
	Pt/Rh	20	2	1384	<2	<2	-1.2	-1.2	-8.9	-8.9
	Ir/Ir50Rh	20	2	1384	<1	<1	-	+3.3	-	+6.7
	Pt/Pt10Rh	15	2	1380	<1	<1	-0.7	-	-6.7	-
	Pt6Rh/Pt30Rh	20	1	1380	-	-	-0.2	-	-1.8	-
	Ir/Ir50Rh	20	2	1380	-	-	+3.8	-	+19.8	-
Norton RA7232	Pt/Pt10Rh	15	2	1380	-	-	-0.6 to -1.1	-0.6 to -1.1	-5.3 to -9.6	-5.3 to -9.6
	Pt/Pt10Rh	15	2	1230	-	-	-0.2	-0.2	-1.7	-1.7
	Pt/Pt10Rh	15	2	1000	-	-	0	0	<0.2	<0.2
	Pt/Pt10Rh	15	2	1380	<1	<1	0	-	<0.2	-
Morganite ΔRR	Pt/Pt10Rh	15	2	1380	<1	<1	0	-	<0.2	-
	Pt/Pt10Rh	15	1	1380	<1	<1	0	-	<0.2	-
	Ir/Ir50Rh	20	2	1380	-	-	+3.9	-	+18.9	-
	Pt/Pt10Rh	15	2	1730	<1	<1	-1.3†	-	-27.5†	-
DeGussit Al23	Pt6Rh/Pt30Rh	20	2	1730	<1	<1	-0.3†	-	-4.0†	-
	Ir/Ir50Rh	20	2	1730	<2	<2	+6.7†	-	+16.9†	-

\*Estimated from data in Fig. 4.

†Instability changes at the reduced temperature of 1380°C.

Instability experiments were made for individual elements and for corresponding welded combinations (after firing at  $1380^{\circ}\text{C}$  and  $1730^{\circ}\text{C}$  in air) to test for junction effects. The magnitude and distribution of emf changes in individually fired wires and in those fired in joined combination were normally identical within reproducibility, and no junction effects were detected beyond an inch from the junction except for thermocouples with pure rhodium in one leg. In these cases, the thermocouples exhibited a rise in emf of the alloy leg joined to the rhodium, which suggested that rhodium migrated out to a distance of approximately 2 inches from the junction.

The influence of time on contamination in air at  $1380^{\circ}\text{C}$  can also be observed from the data in Table 6, where the same couples were checked for instability after firing for 120 and 240 hours. In contrast to the inert atmosphere results, which showed emf changes to be progressive and linear with time (at least to 240 hours), instability values in air for all thermocouples in the Pt-Rh series exhibited no further change after a few hours. Both magnitude and distribution of emf changes in all legs after firing for 240 hours were identical within reproducibility to those measured for 120 hours.

The emf changes generated in Pt and Pt-Rh alloys by contamination in air exhibited very definable delay periods. Instability tests of wires fired for short periods at  $1380^{\circ}\text{C}$  showed that at least 15 to 24 hours were required before any detectable change commenced and that the change was completed in approximately 50 to 60 hours.

Platinum wires, fired in air and argon for 120 hours at  $1380^{\circ}\text{C}$ , were sectioned and compared metallographically. A definite change in structure from the outer edge toward the center was observed for wires fired in air, while a uniform structure was observed for wires fired in argon. This suggests that the initial steps in the contamination with iron are regulated by diffusion rates and solution phenomena. In argon, where the contamination with iron is proceeding at a fast rate, these initial steps probably occur, but were not observed.

Contamination effects in air to  $1400^{\circ}\text{C}$  for individual elements of Pt and Pt-Rh alloys have been shown to be independent of wire size and other geometry effects. Information on the effects of wire size, time, and geometry for Pt-Rh thermocouples at  $1730^{\circ}\text{C}$  and for the Ir/Ir-50%Rh thermocouple was not obtained.

#### Miscellaneous Studies

The resistance of Ir, Ir-50%Rh, and Pt-Rh thermoelements to contamination suggested the possibility of a thermocouple combination involving iridium or the Ir-50%Rh alloy as one leg and a Pt-Rh alloy as the other leg. Although emf versus temperature characteristics of such combinations were favorable, it was found that iridium or some impurity present in iridium strongly contaminated Pt and Pt-Rh alloys. Firing tests at  $1380^{\circ}\text{C}$  for 120 hours in air were conducted for combinations of iridium with Pt and Pt-10%Rh wires. Maximum emf changes at  $860^{\circ}\text{C}$  for Pt and Pt-10%Rh wires near the iridium junctions were as high as 8350 and 1150 microvolts, respectively, and gross contamination extended for several inches above the isothermal zone of the firing furnace. Spectrographic tests indicated a strong pickup of iridium by the other legs. A rapid vaporization of iridium at  $1400^{\circ}\text{C}$  in flowing air was noted at General Electric (9) and was believed to result from a sublimation of the oxide. The high volatility of iridium oxide could explain the gross contamination observed in air. No tests have been performed in a neutral atmosphere.

Error in a thermocouple reading at high temperatures can be caused by an electrical shorting of elements across the sheathing in the region of thermal gradient. A single experiment at  $1700^{\circ}\text{C}$  was made in which a Pt/Pt-10%Rh couple (sheathed in double-bore DeGussit tubing) was joined and compared directly to a bare wire couple, and no significant difference in thermal emf was observed.

## DISCUSSION

The instability results of this study both agree and disagree with past investigations. Chaussain (1), for example, investigated the stability of Pt/Pt-10%Rh thermocouples in various oxide materials at 1300°C in air. The significant emf changes observed with alumina powder for 25-hour periods are not consistent with those in this report, and impurities in the ceramic powder or in the furnace atmosphere may have been responsible for the observed instability.

Ehringer (2) investigated the stability of various Pt and Pt-Rh alloys in powders of pure alumina, aluminum silicate, and silica by firing coiled wires in the powders at 1400°C (air and hydrogen atmospheres). Emf changes observed by Ehringer for wires fired in alumina powder in air are in rough agreement with those reported here for the purer grades of alumina. However, the large emf changes observed for Pt and Pt-6%Rh wires fired for 40 hours at 1400°C in silica powder are not consistent with data in this report and the possibility of the presence of sulfur (10) or other reducing agents may be the cause of this disagreement. McQuillan concluded from experiments with platinum wires and insulation beads at 1600°C that platinum wire may be used in the presence of carbon, beryllia, or alumina, but not in the presence of silicon-bearing materials unless special precautions are taken to eliminate sulfur.

Rudnitskii (3) studied the stabilities of Pt, Rh, and Pt-Rh alloys in air by firing wires at 1350° and 1550°C in alumina sheathing and rechecking the calibrations against platinum at the melting point of copper. Information on the immersion of wires during firing and calibration experiments does not permit a direct comparison of his observed results with those in this report, but the high instabilities reported by him for Pt-Rh alloys are not in agreement with this investigation. The strong contamination may have been due to impurities from the alumina sheathing or from the furnace atmosphere.

Lapp (4) presented data on the stability of Pt, Rh, and Pt-Rh alloys when heated in the presence of alumina and also on the stability of Pt-Rh alloys when heated in powders of alumina, magnesia, and thoria. Wires were fired for short periods of 12 hours at 1500°C in air and checked for emf change by comparison to reference standards at 1000°C. This data is difficult to evaluate because of the short heating periods and lack of information on gradient zones and immersions during the firing and calibration experiments.

Various investigators have studied the volatilization of Pt and Rh (or their oxides) from alloy wires when they are heated in air at temperatures between 1200° and 1600°C, and have disagreed as to which metal is preferentially lost. Bennett (6) has documented this work, and concludes that the losses of Pt and Rh are of a similar order, but that there is a slight preferential loss of Pt. The data in this report show that the preferential loss of either metal is negligible in both air and argon for periods up to 120 hours at temperatures to 1700°C. It must be recognized, however, that the gas was essentially static in these tests, and that any movement of the gas over heated samples would undoubtedly increase any loss due to volatilization.

## CONCLUSIONS

1. The emf instability of a noble metal thermocouple generally results from compositional changes in the thermal gradient zone of one or both elements. When protected thermocouples in the Pt-Rh series are used for extended periods at temperatures between 1000° and 1700°C in either an oxidizing or a neutral atmosphere, compositional changes result mainly from a contamination by impurities from ceramic protection tubes. Contributing effects from the exchange of alloying elements at welded junctions or the preferential volatilization of one metal (or oxide) from alloy legs have been shown to be very small.

2. With alumina sheathing, the principal impurity contributing to instability has been identified as iron. In a neutral atmosphere, the instability generated by the iron contamination is at least one magnitude larger than corresponding changes in an oxidizing atmosphere. When Pt-Rh couples must be used in a neutral atmosphere above 1000°C, or in air above 1200°C, a protective sheathing of low iron content should be used if maximum reliability is required.

3. The instabilities of Pt-Rh thermocouples resulting from contamination by iron in an oxidizing atmosphere (to 1400°C) are shown to be independent of wire size; and the distribution of contaminant along each element is a single function of temperature. On the other hand, in a neutral atmosphere both the degree and distribution of contamination are influenced by wire size, temperature, and other geometry effects. Therefore, larger diameter elements are required for maximum stability in a neutral atmosphere.

4. When thermocouples in the Pt-Rh series are sheathed in alumina and heated for extended periods at temperatures between 1000° and 1700°C, instability increases rapidly with temperature; but the order of instability is fixed for several thermocouples if they are compared at the same temperature, under the same atmosphere, and in the same grade of sheathing. This order of decreasing reliability is as follows: Pt-6%Rh/Pt-30%Rh, Pt-1%Rh/Pt-13%Rh, and Pt/Pt-10%Rh or Pt/Pt-13%Rh.

5. Instability of the pure rhodium thermoelement at 1400°C was found to result mainly from internal changes which occur in the rhodium and only a small part was due to iron contamination. Therefore, the advisability of using thermocouples with pure rhodium in one leg (Pt/Rh and Rh/Pt-20%Rh) is dependent on the iron content of the sheathing and the temperature. Thermocouples with Rh in one leg may be more reliable than other Pt-Rh couples if conditions of use results in gross contamination by iron, or they may be less reliable if minimum contamination conditions exist.

6. Ir and Ir-50%Rh thermoelements also show excellent resistance to contamination by iron; however, both elements appear to exhibit instability by internal changes in the wires. As with rhodium, the reliability of this couple relative to the Pt-Rh thermocouples is dependent on the degree of iron contamination to be expected. For conditions where gross contamination is expected in argon, this couple is potentially more reliable than any of the Pt-Rh couples.

7. If thermocouples are to be used under conditions where compositional changes in either element are expected, the depth of immersion should be maintained constant or increased if maximum reliability is required.

8. If a couple is used under any condition which could lead to contamination, deviations from the original calibration may be expected; and the couple should be periodically checked for induced chemical inhomogeneity along its full length. This can be done very simply by comparing the output of the suspect couple against an unused couple at varying depths of immersion in a long isothermal furnace.

9. The prefiring of Pt and Pt-Rh alloys for 1/2 hour at 1450°C subsequent to calibration and use was shown to be unnecessary for the wires used in this study. However, no positive conclusions should be reached from the small sampling of noble metal wires, since prefiring could effect equalization of any physical or chemical inhomogeneity in a wire and also aid in the removal of any volatile impurities.

The data on contamination and other instability effects presented in this report are by no means complete. Variables such as geometry and purity were difficult to control. Trace impurities in the thermocouple insulation (or the thermoelectric elements) were shown to be important, and variation in purity can be expected in different batches from the same source. All these factors tend to limit the specific application of the data to

practical problems. However, the several generalized conclusions which have been drawn from the data should help to identify and control many sources of error which are encountered when noble metal thermocouples are used to measure temperatures above 1000°C.

#### ACKNOWLEDGMENTS

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Naval Research Laboratory. Report 5792.  
THERMOELECTRIC INSTABILITY OF SOME NOBLE  
METAL THERMOCOUPLES AT HIGH TEMPERATURES,  
by B. E. Walker, C. T. Ewing, and R. R. Miller.  
19 pp. and figs., June 29, 1962.

Thermoelectric instabilities of noble metal thermocouples and individual thermoelements (platinum, rhodium, iridium, iridium-50% rhodium, and several platinum-rhodium alloys) have been studied from 1000° to 1700°C under oxidizing and neutral atmospheres. The principal source of instability was found to be a contamination of the thermoelements by impurities from ceramic protection tubes. Several grades of alumina sheathing were tested, and thermocouple errors associated with each grade were determined.

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1. Thermocouples - Stability
  2. Thermocouples - Thermoelectric properties
  3. Noble metals - Thermoelectric properties
- I. Walker, B. E.  
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